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**Japanese Patent Application JP 3 – 292323 A**

**Method of Producing Polyester**

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**For: Eastman Chemical Company**

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(54) Title of the Invention: **Method of Producing Polyester**

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SPECIFICATION

1. Title of the Invention

Method of Producing Polyester

## 2. Claims

(1) A method of producing polyester, characterized in adding the following type 1, type 2, and type 3 compounds to the polyester production processes when a polyester comprising a bifunctional carboxylic acid that is mainly terephthalic acid, and a glycol that is mainly ethylene glycol is continuously produced, with said first and second compounds being added between the outlet of the esterification reactor and the inlet of the initial polycondensation reactor.

Type 1 compound: At least one compound selected from glycol-soluble magnesium compounds, glycol-soluble manganese compounds, and glycol-soluble zinc compounds

Type 2 compound: At least one compound selected from phosphoric acid, phosphoric acid esters, phosphorous acid, and phosphorous acid esters

Type 3 compound: At least one basic nitrogen compound

(2) The method of producing polyester according to claim (1), characterized in that the type 1, type 2, and type 3 compounds are added so that the following general formulas (I), (II), and (III) are satisfied.

$$1 \leq M \leq 10 \quad [\text{I}]$$

$$0.5 \leq P/M \leq 3 \quad [\text{II}]$$

$$0.2 \leq B \leq 8 \quad [\text{III}]$$

In the formula, M is the amount, represented by the number of moles, of type 1 compound added per 1,000 kg of polyester; P is the amount, represented by the number of moles, of type 2 compound added per 1,000 kg of polyester; and B is the amount, represented by the number of moles, of type 3 compound added per 1,000 kg of polyester.

## 3. Detailed Description of the Invention

### (Field of Industrial Utilization)

The present invention relates to a method of producing polyester, and in particular, to a method of continuously producing by direct polymerization a polyester that is excellently suited for melt film production and produces little coloration and few impurities when made into a film.

(Prior Art)

Polyethylene terephthalate has excellent mechanical strength and chemical stability and is widely used for fibers as well as films for photography, magnetic tape, packaging, capacitors, and the like.

The DMT method whereby dimethyl terephthalate and ethylene glycol serve as the starting materials, and direct polymerization whereby terephthalic acid and ethylene glycol serve as the starting materials ("direct polymerization method" hereafter) are well known as methods of producing polyethylene terephthalate.

Polyester film has often been produced in the past by DMT, but various manufacturers have recently switched to the direct polymerization method in order to reduce manufacturing costs.

Polyester film is usually obtained by melt extrusion with an extruder, followed by uniaxial or biaxial drawing. Adhesion between the cooling drum and the polyester sheet during melt extrusion is an extremely important factor in determining flatness of the film surface. It is known that in order to improve this characteristic, an electrode that applies high voltage is placed between the extruder spinneret and the cooling drum, and a charge is produced on the uncured polyester in order to enhance adhesion with the cooling drum ("electrostatic adhesion" hereafter) (for instance, JP (Kokoku) 37-6142).

However, if the film production speed is increased in order to improve film productivity, the charge that is applied to the uncured sheet is reduced, and there is therefore deterioration of adhesion with the cooling drum, resulting in irregularities in the form of creases and pinholes being made in the surface. The film that is obtained when this type of sheet is drawn has poor surface flatness and cannot withstand actual use, particularly in photography. This phenomenon is particularly obvious with a polyester that is obtained by the direct polymerization method without using a metal catalyst for esterification, as opposed to DMT, which uses large amounts of metal compound as the ester exchange catalyst.

Attempts have been made to add an alkali metal compound or alkaline-earth metal compound to the processes of polyester production in order to increase the amount of charge and

to improve electrostatic adhesion (for instance, JP (Kokai) 51-70269). However, addition of large amounts of these metals to the polyester tends to lead to the generation of very fine aggregate impurities, the secondary production of ether bonds (which reduce the softening point of the polymer), and coloration of the polymer. The polyester that is obtained in this way is difficult to use as a starting material for a polyester film whose quality is sufficient for practical purposes in photography.

The following techniques are disclosed as means for solving this type of problem: those in which an alkali metal and/or alkaline-earth metal compound and a phosphorus compound are added in addition to a metal compound such as a magnesium or manganese compound (for instance, JP (Kokai) 55-84322 and JP (Kokai) 55-89329), and those in which a phosphorus compound and a tertiary amine, quaternary ammonium hydroxide compound, imidazole, a salt thereof, or the like are added in addition to a metal compound such as a magnesium or manganese compound (for instance, JP (Kokai) 55-115425, JP (Kokai) 1-287133). Nevertheless, it was concluded that when polyester is produced by direct polymerization, particularly by a continuous method, process factors such as the order of addition of the above-mentioned types of compounds, the position where they are added, the amount added, the dispersed state of the compounds, and their heat history have a considerable (much more so than with the batch method) effect on coloration and heat resistance of the resulting polyester, and on qualities such as the amount and size of impurities in the polyester, particularly on the level of very fine impurities that are generated when film is made.

#### **(Problems That the Invention Is Intended to Solve)**

A method of continuous production by direct polymerization is proposed for a polyester that has good electrostatic adhesion with the cooling drum during melt film production, is excellently suited for film production, has good heat resistance, shows little coloration, and produces particularly few very fine impurities when made into film.

#### **(Means Used to Solve the Above-Mentioned Problems)**

The above-mentioned object of the present invention is accomplished by a method of producing polyester characterized in adding the following type 1, type 2 and type 3 compounds

to the polyester production process when a polyester comprising a bifunctional carboxylic acid that is mainly terephthalic acid, and a glycol that is mainly ethylene glycol is continuously produced, with the first and second compounds being added between the outlet of the esterification reactor and the inlet of the initial polycondensation reactor.

Type 1 compounds: At least one compound selected from glycol-soluble magnesium compounds, glycol-soluble manganese compounds, and glycol-soluble zinc compounds

Type 2 compounds: At least one compound selected from phosphoric acid, phosphoric acid esters, phosphorous acid, and phosphorous acid esters

Type 3 compounds: At least one basic nitrogen compound

Next, the production method of the present invention will be briefly described citing as an example polyethylene terephthalate and using the conceptual drawing of the device for the continuous production method shown in appended Fig. 1.

A bifunctional carboxylic acid, primarily terephthalic acid, and a glycol, primarily ethylene glycol, are mixed as starting materials in a step 1 reactor for esterification (R-1) to form readily fluidized slurry. The molar ratio of glycol and bifunctional carboxylic acid contained in this slurry should be brought to 1.00 to 1.50 in order to render the slurry fluid and to reduce the amount of the diethylene glycol byproduct. A ratio of 1.05 to 1.25 is particularly preferred.

The mixed slurry is sent to a step 2 reactor for esterification (R-2), and esterified there under increased pressure or normal pressure. Conversion of the starting materials, bifunctional carboxylic acid and glycol, to a slurry and esterification of the slurry are performed in separate reaction vessels.

The esterification reaction is performed under stirring, and the temperature is preferably 240 to 280°C.

The pressure of the reaction system is preferably normal pressure or increased pressure. A pressure of 3 kg/cm<sup>2</sup>G or less is preferred. Esterification will proceed with or without using a particular catalyst. The reaction proceeds as water is removed as a byproduct of the esterification reaction from the distillation column attached to the reaction vessel.

The reaction preferably proceeds until the esterification rate of the reaction product at the outlet of the esterification reactor (R-2) is 95 to 99.9%. The water that has been produced by the step 1 and step 2 esterification reactions is removed from distillation columns (1) and (2).

The esterified product is pumped by a liquid pump (4) and sent to the initial polycondensation reaction process (R-3). However, prior to that, it can be passed through a filter to remove the impurities contained in the reaction liquid. Vertical or horizontal mixing vessels are used for the first polycondensation reaction.

The initial polycondensation reaction product is then [reacted] in the intermediate polycondensation reactor (R-4) and final polycondensation reactor (R-5) to increase the degree of polymerization and to produce a polyester polymer with a number-average degree of polymerization of about 100. There are also cases wherein the intermediate polycondensation reactor is dispensed with because of restrictions related to the required quality of the polymer, facility cost, and the like.

The final polycondensation reactor is generally constructed using a horizontal biaxial mixing vessel and is operated at a temperature of 270 to 290°C and a pressure of 0.1 to 2 Torr.

The first, (intermediate), and final polycondensation reactors are decompressed using a vacuum generation source (3).

The emission pressure of the pump that feeds the esterification product to the initial polycondensation reaction process (R-3) is adjusted by means of a pressure control valve (5). The polycondensation catalyst is preferably added before the polycondensation reaction starts.

The type 1, type 2, and type 3 compounds, which are characteristic of the method of the present invention, are added through an addition port such as that shown in appended Fig. 2 in a step in which the materials are fed to the initial polycondensation reactor from the esterification reaction system. (Although the case where there is a two-step addition port, No. 1 and No. 2, is shown in Fig. 2, it is also possible to use No. 1 alone.)



If both type 1 and type 2 compounds are present for a long period of time in the esterification reaction liquid before polycondensation actually starts, these compounds will react to form a metal salt of phosphoric acid that will precipitate as an impurity in the polymer.

In addition, type 2 compound is generally volatile, and even minimal fluctuations in the process will result in large fluctuations in the amount remaining in the polymer, often leading to variations in quality, such as transparency, coloration, heat resistance, and the like.

A variety of methods can be used for mixing and adding the above-mentioned type 1 and type 2 compounds separately (and sometimes the type 3 compound at the same time), or for mixing and adding two or more types of compounds, but what is important is that they are added to the esterification reaction product in a state in which polycondensation will be virtually absent at a temperature of 280°C or less and an absolute pressure of 1.0 kg/cm<sup>2</sup> or higher, and that the mean time it takes the reactants to reach the initial polycondensation reactor after being uniformly dispersed, dissolved, and added by mixing under force is 10 minutes or less, and preferably 5 minutes or less.

When a specific example of the mixing method of the present invention is recited in accordance with Fig. 2, a pump (4) for pumping the esterification reaction product, an inline mixer (8), and a pressure control valve (5) are placed in that order between the esterification reactor (R-2) and initial polycondensation reactor (R-3). Ports (6) and (7) for introducing additives are disposed between the pump and the inline mixer, and the desired purpose can be achieved by introducing type 1 and type 2 compounds through these addition ports. The position of the ports is selected so that the mean retention time up to the initial polycondensation reactor is 10 minutes or less, and preferably 5 minutes or less, and it is preferred that the inline mixer be directly behind the addition ports. The pressure control valve is set up so that the emission pressure of the pump is equal to an absolute pressure of 1.0 kg/cm<sup>2</sup> or higher. Multiple ports can be set up for introducing the additives, and type 1 and 2 compounds can be separately introduced. A high-shear inline mixer, such as a static mixer, is preferred.

Various modifications of the methods described above, or completely different methods may also be suggested, and the present invention is not limited by the individually appended embodiments.

Organic carboxylates (such as acetates, oxalates, and benzoates), halides, hydroxides, and the like can be cited as the glycol-soluble magnesium compound, glycol-soluble manganese compound, and glycol-soluble lead compound used in the present invention.

Specific examples include magnesium acetate, magnesium oxalate, magnesium chloride, magnesium bromide, magnesium hydroxide, manganese acetate, manganese oxalate, manganese chloride, manganese bromide, manganese hydroxide, zinc acetate, zinc oxalate, zinc chloride, zinc bromide, zinc hydroxide, and the like.

Phosphorous acid, phosphoric acid, trimethyl phosphate, triethyl phosphate, triphenyl phosphate, mono- or di-esters of phosphoric acid or phosphorous acid, and the like can be cited as specific examples of suitable phosphorus compounds. Imidazole, imidazole derivatives, imidazoline, imidazoline derivatives, ketamine, ketamine derivatives, theta-oxazine, para-oxazine, and their salts in the form of oxalates, hydrochlorides, aliphatic carboxylates, and the like can be cited as specific examples of suitable basic nitrogen compounds.

A polyester of the desired quality is obtained when the amount of type 1, type 2, and type 3 compounds added satisfies the correlation shown by the following general formulas [I], [II], and [III].

$$1 \leq M \leq 10 \quad [I]$$

$$0.5 \leq P/M \leq 3 \quad [II]$$

$$0.2 \leq B \leq 8 \quad [III]$$

The present invention can also be applied to polyesters containing, in addition to polyethylene terephthalate, 20% or less of a copolymerization component. Aromatic dicarboxylic acids such as isophthalic acid; aliphatic dicarboxylic acids such as cyclohexanedicarboxylic acid, adipic acid, and sebacic acid; and the like can serve as such copolymerization components. Diethylene glycol, triethylene glycol, butanediol, cyclohexamethanediol, xylene glycol, and the like can be cited as glycol components suitable as such copolymerization components.

### (Working Examples)

In order to clarify the embodiments and effect of the present invention, a conventional case (Comparative Example 1) and the method of the present invention (Working Example 1) will be used to describe in detail the addition of additives during the production of polyester. It is apparent, however, that the present invention is not limited by the specific examples described below.

#### (Comparative Example 1)

Esterification was performed as a 68:166 (weight ratio) mixed slurry of ethylene glycol and terephthalic acid was continuously fed at 1,000 parts by weight per hour to the continuous polyester production device shown in Fig. 1.

Esterification was performed under atmospheric pressure at 255°C, and the water byproduct was continuously removed from the distillation column.

Antimony trioxide as the polymerization catalyst was continuously fed at 0.17 parts by weight per hour to esterification reactor (R-1) together with the slurry of ethylene glycol and terephthalic acid.

A 5-wt% ethylene glycol solution of magnesium citrate tetrahydrate was added at 12 parts by weight per hour, and a 5-wt% ethylene glycol solution of trimethylphosphate was added at 4 parts by weight per hour to the esterification second reactor (R-2).

Initial polycondensation reactor (R-3) was operated at a pressure of 45 mmHg and a temperature of 270°C.

A 0.5-wt% ethylene glycol solution of 1,4-diazabicyclo(2,2,2)octane was added at 6.6 parts by weight per hour to (R-3).

Final polymerization reactor (R-5) was operated at a temperature of 280°C and a pressure of 1.2 mmHg to produce 820 parts by weight of polymer per hour.

The ethylene glycol that was produced by the polycondensation reaction was discharged outside the system together with the condensation water of a steam ejector as the vacuum generation source.

The polymer that was obtained had a limiting viscosity, as determined with a mixed solution of phenol and tetrachloroethane (1:1 weight ratio), of 0.65. It was excellently suited for film production and there was little coloration due to pyrolysis. However, when made into a film with a thickness of 75  $\mu\text{m}$ , impurities that contained elemental magnesium and were 5  $\mu\text{m}$  or larger were found at an average of 12 impurities per 15 cm  $\times$  15 cm.

According to a fluorescent X-ray analysis, the phosphorus atom content of the polymer was 30 ppm.

(Working Example 1)

As shown in Fig. 2, an additive feed port was attached to the piping that connected the esterification second reactor (R-2) and initial polycondensation reactor (R-3) of a polyester production device having the same structure as in Comparative Example 1, and an inline mixer was placed directly behind. Additives that were added from the addition port were mixed with the esterification reaction product as they were being sent to the initial polycondensation reaction. The retention time up to the initial polycondensation reactor inlet was 4 minutes.

The magnesium acetate was a liquid of the same concentration as in Comparative Example 1, and the trimethyl phosphate was 75% of that in Comparative Example 1. This was added from the above-mentioned addition port at a ratio of 3 parts by weight per hour. The esterification reaction conditions and the polycondensation reaction conditions were the same as in Comparative Example 1.

The polymer that was obtained had a limiting viscosity of 0.65. As with Comparative Example 1, it was excellently suited for film production and showed little coloration due to pyrolysis. When a film with a thickness of 75  $\mu\text{m}$  was made, at first glance it was no different from the film obtained using the polymer of the comparative example. However, impurities that contained elemental magnesium and were 5  $\mu$  or larger were only seen an average of 1.5 impurities per 15 cm  $\times$  15 cm.

Moreover, even though little trimethyl phosphate was added, the phosphorus atom content in the polymer according to a fluorescent X-ray analysis was on the same level (at 31 ppm) as that of Comparative Example 1.

The characteristics of the polymers that were obtained in Comparative Example 1 and Working Example 1 are summarized in the following Table 1.

Table 1

	Limiting viscosity	b-value of polymer	Number of impurities in film	Content of phosphorus atoms
Comparative Example 1	0.65	3.2	12	30 ppm
Working Example 1	0.65	3.3	1.5	31 ppm

#### (Effect of the Invention)

By adding type 1, type 2, and type 3 compounds in accordance with the method of the present invention during continuous production of polyester by direct polymerization, it is possible to produce a polyester that shows good electrostatic adhesion to the cooling drum during melt film production, is excellently suited for film production, has good heat resistance, shows little coloration, and produces particularly few fine impurities when made into film. With this polyester, it is possible to produce film substrates for microfilm as well as photographic film for original prints, which must be high quality.

#### 4. Brief Description of the Drawings

Appended Fig. 1 shows a conventional device for continuous production of polyester by the direct polymerization method.

In the figure,

R-1 is the step 1 reactor for esterification,

R-2 is the step 2 reactor for esterification,

R-3 is the initial polycondensation production device,

R-4 is the intermediate polycondensation production device,

R-5 is the final polycondensation production device,

(1) and (2) are distillation columns, (3) is the vacuum generation source,  
(4) is the esterification product pump, and  
(5) is the pressure control valve.

Appended Fig. 2 shows a typical continuous polyester production device suitable for the method of the present invention.

In the figure,

R-2 is the step 2 reactor for esterification,  
R-3 is the initial polycondensation reaction device,  
(4) is the esterification product pump,  
(5) is the pressure control valve,  
(6) and (7) are addition ports No. 1 and No. 2,  
(8) is the inline mixer, and  
(9) and (10) are the check valves.

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Fig. 1

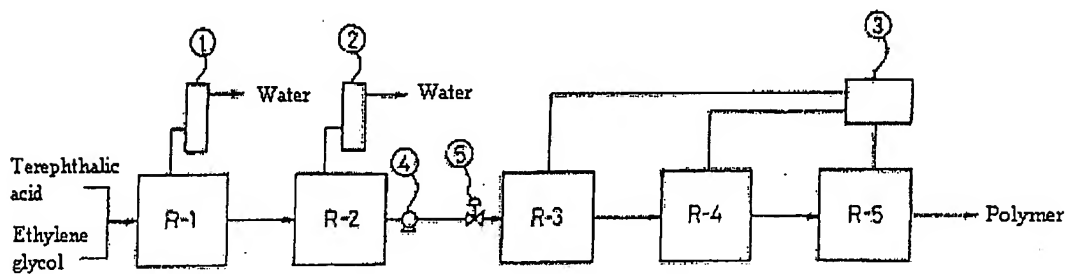


Fig. 2

